# Using the Agilent 6890 Gas Chromatograph and Agilent 5973 Mass Spectrometer System for EPA Method 524.2

Application

Gas Chromatography


## Authors

James Refermat and
Marcell Stephens
Quanterra Incorporated
5910 Breckenridge Parkway,
Suite H
Tampa, FL 33610
USA

Mike Szelewski
Agilent Technologies, Inc.
2850 Centerville Road
Wilmington, DE 19808
USA



## Abstract

**A system comprised of a purge and trap (P&T) concentrator, a gas chromatograph (GC), and a mass spectrometer (MS) was used to determine 61 volatile organic compounds (VOCs). All U.S. EPA method 524.2 criteria were met without using cryofocusing. The P&T and GC-MS conditions listed in tables 1 and 2 detail the instrument settings. The method development for analyzing 524.2 analytes was refined by members of the GC-MS Volatile Organics Analysis (VOA) group at Quanterra in Tampa, Florida.**


## Introduction

U.S. EPA method 524.2 is a general-purpose method used to identify and quantify volatile organic compounds (VOCs) in surface, ground, and drinking water. The method is applicable to a wide range of organic compounds including the four trihalomethane disinfection byproducts. The 61 VOCs in this note are a subset of the 84 VOCs that can be analyzed using method 524.2.

Compounds of sufficient high volatility and low water solubility are purged from a water sample using helium and trapped on a solid sorbant held at room temperature. At the end of the purge cycle, the trap is heated and, using helium, the compounds are desorbed onto the head of a gas chromatograph (GC) column. The GC column is temperature programmed, and the analytes are eluted into the mass spectrometer (MS) ion source. The MS is used for identification and measurement. The purge and trap (P&T)-GC-MS system is controlled from a PC.

## Experimental

The program requirements for which the 524.2 analysis is used must meet local state regulatory guidelines as well as EPA method 524.2 acceptance criteria and U.S. Air Force compliance guidelines under the auspices of the Air Force Center for Environmental Excellence (AFCEE) program.

Quanterra maintains strict QA/QC procedures at all 12 facilities. Each location has a quality assurance officer (QAO) reporting directly to the corporate quality assurance director. Quanterra's network of 12 facilities in 10 states staffs over 700 employees and encompasses over 310,000 square feet of facility space, providing the capacity to handle any analytical need. Quanterra performs more than 1.5 million separate tests per year. A nationwide network of fully equipped labs, linked by advanced information management systems, assures a high standard of testing and consistent quality.

Quanterra's comprehensive quality management system (QMS) forms the foundation of their quality goals. Quanterra's QMS ensures that their clients receive high-quality analytical services that are timely and reliable, and that meet the intended purpose in a cost-effective manner. The QMS also applies to all Quanterra technical, business, and administrative functions. The principles and practices expounded in the QMS apply to all staff and are fundamental to the services they provide. As a result, Quanterra is continuously seeking ways to improve their products and services using the best technologies available. The AGILENT 6890 / AGILENT 5973 GC-MS system provides high-quality data and increased productivity.

The P&T instrumentation and conditions are listed in table 1. The Vocarb 3000 trap allows for higher desorb and bake temperatures. The high desorb temperature facilitates efficient desorption of target analytes, and the high bake temperature minimizes carryover between samples. The standard transfer line provided with the P&T was replaced with a Restek 0.53-mm SilcoSteel MXT 502.2 column. The use of the analytical column as the transfer line between the P&T and GC appears to improve peak symmetry for low-level standards. The transfer line is attached directly to the AGILENT 6890 GC injection port (direct capillary interface) and runs in the split mode. A purge rate of 50 mL/min appears to improve the recovery of analytes that are known to have poor purge efficiencies. The 50-mL/min purge flow did not have an adverse effect on the recovery of the gases and, as a result, produced method and program compliant data. Traditional trap packing materials (Tenax/charcoal/ silica) usually did not hold the gases at higher purge flow rates, resulting in poor recoveries. This problem was not observed when using the Vocarb 3000 trap. The original method's desorb and bake temperature of 180 °C is a limitation associated with traditional packing material (Tenax break down).

The GC-MS instrumentation and conditions are listed in table 2. Conditions were optimized for maximum sample throughput while meeting site-specific data quality objectives. The split ratio used allows the best combination of sensitivity and peak shape. With this configuration, it is advantageous to use the electronic pressure control (EPC) inlet (option available on the AGILENT 6890 GC). With the EPC inlet pressure on, the chromatography for the gases is improved, and analytes at the end of the temperature program have much sharper peak shape. EPC also gives much better reproducibility of analyte retention times.

Each 12-hour shift (site-specific requirements allow for a 12-hour clock for the tune verification) starts with verification of the fragmentation pattern of 4-bromofluo-robenzene (BFB) obtained from 25 ng on-column. A five-point calibration curve is then analyzed at concentrations of 500, 250, 125, 50, and 12.5 ng on-column. Once the calibration acceptance criteria is verified, a 100-ng (4 µg/L) laboratory control spike/laboratory control spike duplicate (LCS/LCSD) is analyzed followed by a method blank. Successful analysis of

**Table 1. Purge and Trap Conditions**

| | |
|---|---|
| P&T | Tekmar LSC 3000 |
| Automatic sampler | Tekmar ALS 2016 |
| Trap | Vocarb 3000 Supelco part no. 2-4920 |
| P&T-GC interface | Custom* |
| Sample size | 25 mL |
| Purge temperature | 35 °C |
| Purge rate | 50 mL/min |
| Purge time | 11 min |
| Dry purge time | 1 min |
| Desorb preheat temperature | 250 °C |
| Desorb temperature | 260 °C |
| Desorb time | 2 min |
| Bake temperature | 270 °C |
| Bake time | 6 min |
| Bake-gas bypass on time | 1 min |
| Line/valve temperature | 100 °C |
| Water management control (WMC) temperature | 310 °C |

*Standard transfer line replaced with approximately 0.7-m length of Restek MXT-502.2 SilcoSteel 0.53-mm id column

**Table 2. Gas Chromatograph and Mass Spectrometer Conditions**

| **Gas chromatograph** | **Agilent 6890** |
|---|---|
| Inlet | EPC split/splitless |
| Mode | Split |
| Inlet temperature | 200 °C |
| Pressure | 13.9 psi |
| Split ratio | 35:1 |
| Split flow | 24.2 mL/min |
| Gas saver | On at 2 min |
| Gas saver flow | 20.0 mL/min |
| **Oven** | |
| Initial temperature | 35 °C |
| Initial time | 4 min |
| Rate | 15 °C/min |
| Final temperature | 200 °C |
| Final time | 0.1 min |
| Equilibration time | 0.5 min |
| Oven max temperature | 240 °C |
| **Column** | **DB-624 fused silica capillary** |
| Agilent equivalent | Agilent part no. 121-1324 |
| Length | 20 m |
| Diameter | 180 µm |
| Film thickness | 1.0 µm |
| Initial flow | 0.7 mL/min |
| Average velocity | 37.0 cm/sec |
| Mode | Constant flow |
| Inlet | Front |
| Outlet | MS |
| Outlet pressure | Vacuum |
| **Mass spectrometer** | **Agilent 5973** |
| Solvent delay | 1.1 min |
| EM voltage | 2035 volts |
| Low mass | 35 amu |
| High mass | 260 amu |
| Threshold | 200 |
| Sampling | 3 |
| Scans/sec | 3.25/sec |
| Quad temperature | 150 °C |
| Source temperature | 200 °C |
| Transfer line temperature | 250 °C |

the LCS/LCSD and blank are followed by 20 field samples. A typical instrument sequence, when initial calibration is not required, is shown in table 3. This new sample sequence starts with an instrument tune verification (BFB analysis) followed by the analysis of the continuing calibration verification (CCV) standard, If the CCV fails, the system is recalibrated. After the CCV, a 100-ng (4 µg/L) LCS/LCSD is analyzed followed by a method blank and 20 field samples. *The LCS/LCSD QC samples are a site-specific project requirement.*

**Note:** The AGILENT 5973 MS only required retuning every 4 to 6 weeks during large sampling events. During these events, 26 samples were analyzed every 12 hours, operating 6 to 7 days a week.

## Results

The results from the BFB tuning analysis are shown in table 4, together with the EPA method 524.2 tuning criteria. If the BFB tuning criteria are not met, typically mass 50 was low or mass 176 was high. The problem was resolved by running the auto-tune option provided with the Enviro-Quant software followed by a reanalysis of the BFB solution. If the BFB still did not pass, the problem was resolved by replacing the trap. The AGILENT 5973 MS ran for over a year before there was a need to open the analyzer and replace the filaments. The source was cleaned while the analyzer was open, and a little scorching around the filament area was observed. SW-846 method 8260B and CLP-SOW Method OLC02.1 were also performed using this instrument, often containing high levels of target and non-target analytes. As a result, finding the source and its component parts in good condition was unexpected.

A list of target analytes for this project, together with their compound number and retention time (RT), are shown in table 5. The method detection limits (MDLs) shown are based on initial calculations per 40 CFR, Part 136, Appendix B. Prior to running client samples, an instrument detection limit (IDL) study was conducted. This comprised of a five-point calibration curve followed by the CCV, method blank, and seven replicates of the 0.5-µg/L standard for 7 consecutive days. The results between replicates within the same analytical

**Table 3. Instrument Sequence**

| **Sequence No.** | **Description** |
|---|---|
| 1 | 1 ppb BFB, with CCV |
| 2 | 10 ppb CCV |
| 3 | 4 ppb LCS |
| 4 | 4 ppb LCSD |
| 5 | Method blank |
| 6 | Sample 1 |
| 7 | Sample 2 |
| ⋮ | ⋮ |
| | Matrix spike |
| | Matrix spike duplicate |
| | ⋮ |
| 27 | Sample 20 |

**Table 4. BFB Tuning Criteria and Results**

| m/e | Ion Abundance Criteria | Ion Abundance Results |
|---|---|---|
| 95 | Base Peak, 100% relative abundance | 100.00 |
| 50 | 15.00%-40.00% of mass 95 | 19.26 |
| 75 | 30.00%-60.00% of mass 95 | 46.39 |
| 96 | 5.00%-9.00% of mass 95 | 7.25 |
| 173 | Less than 2.00% of mass 174 | 0.65 |
| 174 | Greater than 50.00% of mass 95 | 85.07 |
| 175 | 5.00%-9.00% of mass 174 | 7.45 |
| 176 | 95.00%-101.00% of mass 174 | 100.70 |
| 177 | 5.00%-9.00% of mass 176 | 6.89 |

sequence demonstrated very little variation. Additionally, the results obtained between the day-to-day analytical sequences also exhibited very little variation. The IDL study and the MDL study yielded similar results with little or no statistical variation. All analyte MDLs are comfortably below the 0.5 µg/L reporting limit for this project. Lower detection limits could be achieved with lower split ratios.

The initial calibration for this set of analyses was done in August 1997 at the following five levels: 0.5, 2.0, 5.0, 10, and 20 µg/L. Response factors were calculated for each analyte at each level. The percent relative standard deviations (%RSDs) of these response factors, listed in table 5, are all less than 20 and meet the criteria for Table 5. Target Compound List with QA\QC (continued) linearity. Hexachlorobutadiene and naphthalene had trouble meeting the daily ICV/CCV acceptance criteria on a daily basis; these compounds are known as poor purgers. Fortunately, the site-specific QA requirements allows for the use of a quadratic calibration when the acceptance criteria for linearity is not met.

**Table 5. Target Compound List with QA\QC**

| Compound Number | Compound Name | RT | MDL | Init Cal %RSD RRF limit 0-20 | CCV %D limit ± 30 | LCS %Rec limit 70-130 | LCSD %RPD limit 0-20 |
|---|---|---|---|---|---|---|---|
| *Internal Standard* | | | | | | | |
| 36 | Fluorobenzene | 6.651 | | | | | |
| *Surrogates* | | | | | | | |
| 63 | 4-Bromofluorobenzene | 10.919 | | 5.23 | -12. | 99.8 | 2.0 |
| 33 | 1,2-Dichlorobenzene-d(4) | 12.436 | | 6.54 | -1.9 | 105. | 7.6 |
| *Target Analytes* | | | | | | | |
| 34 | Benzene | 6.322 | 0.18 | 8.64 | 3.9 | 94.8 | 6.8 |
| 64 | Bromobenzene | 11.065 | 0.15 | 3.72 | -12 | 112. | 5.5 |
| 27 | Bromochloromethane | 5.574 | 0.19 | 15.5 | -1.3 | 104. | 2.1 |
| 40 | Bromodichloromethane | 7.592 | 0.21 | 10.1 | -0.9 | 100. | 5.0 |
| 61 | Bromoform | 10.595 | 0.23 | 15.3 | -21. | 111. | 5.3 |
| 6 | Bromomethane | 1.907 | 0.31 | 13.4 | 4.7 | 82.3 | 1.8 |
| 79 | n-Butylbenzene | 12.451 | 0.19 | 10.7 | -11. | 97.2 | 8.3 |
| 74 | sec-Butylbenzene | 11.897 | 0.19 | 9.47 | -8.5 | 98.7 | 12. |
| 72 | tert-Butylbenzene | 11.682 | 0.20 | 6.21 | 3.0 | 110. | 12. |
| 31 | Carbon tetrachloride | 6.091 | 0.17 | 10.0 | -5.3 | 104. | 7.8 |
| 55 | Chlorobenzene | 9.784 | 0.17 | 6.67 | -4.0 | 105. | 3.0 |
| 7 | Chloroethane | 2.007 | 0.18 | 6.51 | 9.9 | 82.8 | 4.2 |
| 29 | Chloroform | 5.699 | 0.18 | 7.47 | 6.1 | 97.0 | 1.8 |
| 4 | Chloromethane | 1.510 | 0.19 | 6.77 | 16. | 75.6 | 8.4 |
| 69 | 2-Chlorotoluene | 11.264 | 0.18 | 6.53 | -9.4 | 103. | 7.1 |
| 71 | 4-Chlorotoluene | 11.369 | 0.17 | 7.55 | -11. | 105. | 7.6 |
| 51 | Dibromochloromethane | 9.188 | 0.17 | 11.1 | -12. | 108. | 0.04 |
| 81 | 1,2-Dibromo-3-Chloropropane | 13.215 | 0.30 | 6.44 | 16. | NR | NR |
| 52 | 1,2-Dibromoethane | 9.287 | 0.25 | 13.3 | 9.2 | 95.1 | 8.0 |
| 39 | Dibromomethane | 7.404 | 0.24 | 14.0 | 8.4 | 111. | 1.0 |

**Table 5. Target Compound List with QA\QC (continued)**

| Compound Number | Compound Name | RT | MDL | Init Cal %RSD RRF limit 0-20 | CCV %D limit ± 30 | LCS %Rec limit 70-130 | LCSD %RPD limit 0-20 |
|---|---|---|---|---|---|---|---|
| *Target Analytes (continued)* | | | | | | | |
| 80 | 1,2-Dichlorobenzene | 12.451 | 0.19 | 7.44 | -0.4 | 104. | 3.2 |
| 76 | 1,3-Dichlorobenzene | 11.996 | 0.20 | 8.36 | -2.5 | 105. | 3.3 |
| 78 | 1,4-Dichlorobenzene | 12.090 | 0.17 | 8.84 | 0.3 | 99.8 | 2.8 |
| 3 | Dichlorodifluoromethane | 1.353 | 0.21 | 6.07 | 15. | 83.3 | 9.1 |
| 22 | 1,1-Dichloroethane | 4.475 | 0.22 | 7.82 | 11. | 88.7 | 5.3 |
| 35 | 1,2-Dichloroethane | 6.342 | 0.20 | 11.2 | 5.3 | 99.8 | 3.5 |
| 12 | 1,1-Dichloroethene | 2.280 | 0.20 | 7.61 | 8.5 | 99.0 | 6.4 |
| 25 | cis-1,2-Dichloroethene | 5.275 | 0.22 | 8.63 | -6.3 | 97.2 | 3.6 |
| 18 | trans-1,2-Dichloroethene | 3.842 | 0.17 | 10.9 | 13. | 94.8 | 4.9 |
| 38 | 1,2-Dichloropropane | 7.284 | 0.22 | 10.0 | 8.6 | 88.3 | 2.1 |
| 49 | 1,3-Dichloropropane | 8.957 | 0.12 | 6.56 | 7.4 | 95.7 | 0.76 |
| 24 | 2,2-Dichloropropane | 5.265 | 0.20 | 9.39 | 4.2 | 92.6 | 0.80 |
| 32 | 1,1-Dichloropropene | 6.097 | 0.18 | 9.13 | 5.0 | 88.3 | 12. |
| 42 | cis-1,3-dichloropropene | 8.053 | 0.19 | 10.5 | 2.3 | 95.0 | 0.64 |
| 46 | trans-1,3-dichloropropene | 8.618 | 0.14 | 10.6 | 5.1 | 95.0 | 3.3 |
| 56 | Ethylbenzene | 9.904 | 0.20 | 8.46 | 3.9 | 89.4 | 8.6 |
| 83 | Hexachlorobutadiene | 14.229 | 0.24 | 16.1 | -4.5 | 90.6 | 5.7 |
| 62 | Isopropylbenzene | 10.778 | 0.17 | 9.23 | 0.6 | 98.4 | 10. |
| 75 | 4-Isopropyltoluene | 12.049 | 0.20 | 9.07 | 11. | 102. | 8.9 |
| 16 | Methylene chloride | 3.445 | 0.21 | 9.07 | -3.5 | 109. | 5.0 |
| 98 | Methyl-t-butyl ether | 3.884 | 0.20 | 10.4 | 8.3 | 97.7 | 3.0 |
| 84 | Naphthalene | 14.287 | 0.13 | 19.7 | 5.3 | 76.8 | 5.8 |
| 67 | n-Propylbenzene | 11.186 | 0.21 | 6.92 | -16. | 108. | 7.7 |
| 60 | Styrene | 10.422 | 0.18 | 11.8 | -0.3 | 96.4 | 5.8 |
| 57 | 1,1,1,2-Tetrachloroethane | 9.868 | 0.21 | 8.27 | -5.3 | 102. | 10. |
| 65 | 1,1,2,2-Tetrachloroethane | 11.065 | 0.18 | 6.57 | -2.4 | 101. | 4.8 |
| 48 | Tetrachloroethene | 8.942 | 0.21 | 8.61 | 8.6 | 89.0 | 10. |
| 45 | Toluene | 8.393 | 0.14 | 9.37 | -6.7 | 102. | 9.6 |
| 85 | 1,2,3-Trichlorobenzene | 14.528 | 0.18 | 9.13 | 0.7 | 90.7 | 5.5 |
| 82 | 1,2,4-Trichlorobenzene | 14.052 | 0.16 | 11.0 | -1.7 | 91.7 | 3.6 |
| 30 | 1,1,1-Trichloroethane | 5.893 | 0.24 | 8.34 | -2.9 | 102. | 6.3 |
| 47 | 1,1,2-Trichloroethane | 8.795 | 0.17 | 12.3 | 4.3 | 105. | 1.2 |
| 37 | Trichloroethene | 7.059 | 0.16 | 8.77 | -4.6 | 100. | 6.7 |
| 9 | Trichlorofluoromethane | 2.273 | 0.19 | 5.26 | 6.2 | 99.1 | 3.9 |
| 68 | 1,2,3-Trichloropropane | 11.102 | 0.20 | 5.54 | 2.7 | 101. | 8.8 |
| 73 | 1,2,4-Trimethylbenzene | 11.729 | 0.17 | 8.38 | 2.0 | 95.7 | 7.6 |
| 70 | 1,3,5-Trimethylbenzene | 11.363 | 0.18 | 9.42 | 0.3 | 94.7 | 9.4 |
| 5 | Vinyl chloride | 1.609 | 0.15 | 7.54 | 4.4 | 82.1 | 13. |
| 59 | o-Xylene | 10.411 | 0.13 | 10.7 | 0.3 | 94.0 | 7.5 |
| 58 | m-Xylene | 10.019 | 0.17 | 8.15 | 2.8 | 92.6 | 9.3 |
| 58 | p-Xylene | 10.019 | 0.17 | 8.15 | 2.8 | 92.6 | 9.3 |

After the BFB tuning verification is performed, a CCV is run at the 10-ppb level. The method requires that each analyte response factor (RF) is ± 30% of its initial calibration value. These percent deviations (%Ds) are listed in table 5, and all analytes meet the method criteria. If one or more analytes do not meet this criteria, a new five-point calibration curve is run. The data presented here were run in September 1997, one month after the initial calibration. This system is very stable for long periods of time. A five-level calibration has only been necessary eight to ten times in the last 12 months. A total ion chromatogram (TIC) for the CCV is shown in figure 1.

This project requires analysis of a LCS and LCSD. Laboratory blank water is spiked at the 4-µg/L level and analyzed in duplicate. The recoveries for each analyte must be between 70% and 130% for each analyte. A duplicate aliquot of the LCS, referred to as an LCSD, is then analyzed. The relative percent difference (RPD) of this LCS and the LCSD must be less than 20% for each analyte. The LCS recoveries and LCSD RPDs are shown in table 5. All analytes met the site-specific acceptance criteria.

After all of the project-specific QA/QC requirements are met, actual field samples can be analyzed. Results for three samples are shown in table 6. The samples were taken from private wells in an Area of Concern (AOC) in the northeast United States. All ion profiles met the site-specific QC acceptance criteria and all other regulatory acceptance criteria for this AOC.

A TIC for sample 1 is shown in figure 2. The excellent peak shape is typical of the system performance in our laboratory.

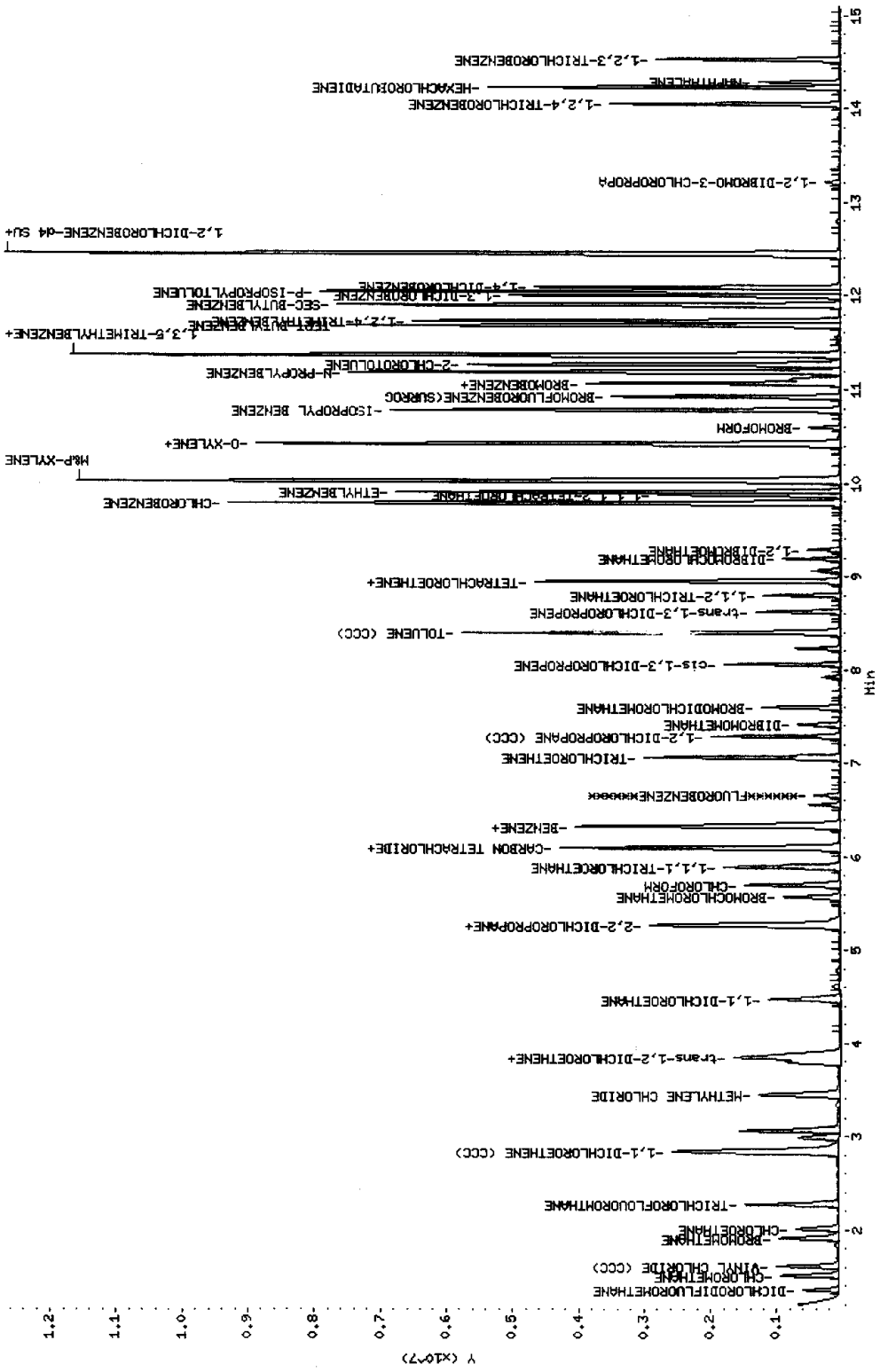


**Figure 1. CCV total ion chromatogram.**

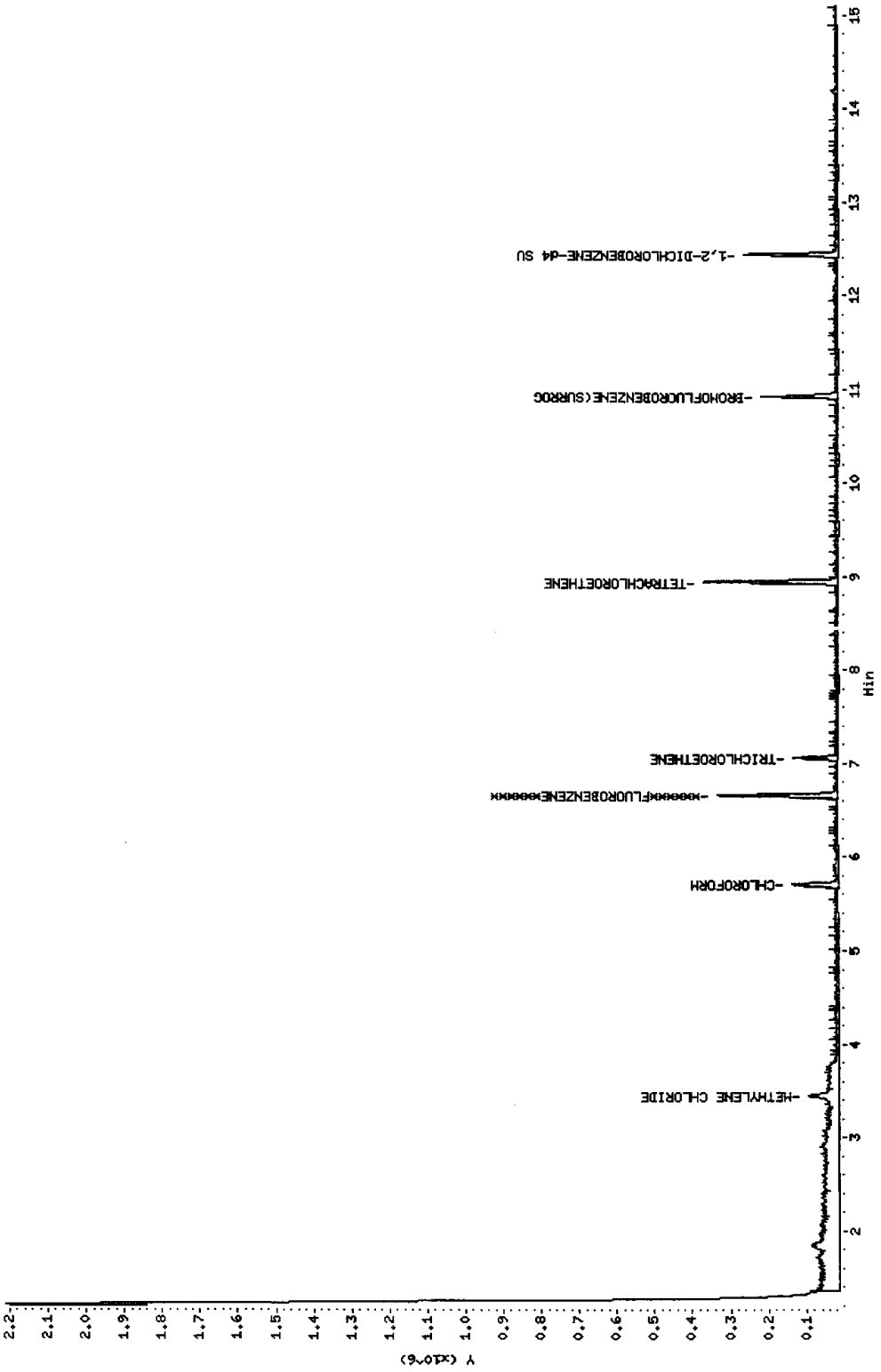


**Figure 2. Total ion chromatogram for field sample one.**

**Table 6. Results of Sample Analyses**

| Compound Number | Compound Name | RT min | Sample1 | Sample2 | Sample 3 |
|---|---|---|---|---|---|
| *Internal Standard* | | | | *Area % Difference limit ± 30* | |
| 36 | Fluorobenzene | 6.651 | -25.6 | -29.2 | -18.65 |
| *Surrogate Standards* | | | | *% Rec 1.0 ppb limit 80-100* | |
| 33 | 1,2-Dichlorobenzene-d(4) | 12.436 | 98.7 | 99.5 | 95.1 |
| 63 | 4-Bromofluorobenzene | 10.919 | 85.2 | 93.4 | 89.0 |
| *Target Analytes* | | | *[ppb]* | *[ppb]* | *[ppb]* |
| 16 | Methylene chloride | 3.445 | 0.55 | 0.56 | 1.0 |
| 29 | Chloroform | 5.699 | 1.0 | 3.7 | 1.0 |
| 37 | Trichloroethene | 7.059 | 0.54 | < 0.50 | < 0.50 |
| 40 | Bromodichloromethane | 7.592 | < 0.50 | 5.9 | 2.3 |
| 48 | Tetrachloroethene | 8.942 | 1.2 | < 0.50 | < 0.50 |
| 51 | Dibromochloromethane | 9.188 | < 0.50 | 8.4 | 5.1 |
| 61 | Bromoform | 10.595 | < 0.50 | 2.7 | 3.2 |

## Conclusions

The AGILENT 6890/AGILENT 5973 GC-MS can be used to perform EPA method 524.2. All calibration, verification, and quality control criteria of the method can be met on a routine basis. The system exhibits excellent stability, minimal downtime, and sufficient sensitivity to meet the requirements for this project. The system performance, combined with expert personnel and a rigorous QA/QC program, results in high sample throughout for method 524.2. The AGILENT 6890/ AGILENT 5973 GC-MS allows Quanterra to meet clients' expectations in a timely and cost-effective manner.

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Printed in the USA
April 26, 2001
5968-1257E

Agilent Technologies